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Nuclear spin-lattice relaxation of I = 3/2 quadrupolar spin-system due to domain-walls in order-disorder ferroelectrics

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Abstract : A general theory is developed for the study of spin-lattice relaxation of I = 3/2 spins due to domain-walls in order-disorder ferroelectrics. It is assumed that the domain-wall structure is responsible for relaxation and the transfer of nuclear magnetization between the nuclei near the domain walls and those deep inside the domain occurs through nearest neighbour interaction by spin-diffusion process. Rate equations are formed by representing the ferroelectric domains by a one-dimensional chain of equidistant spins having dipolar coupling. Spin-populations are calculated as a function of time for different ratios of quadrupolar to dipolar transition probabilities for a sample subjected to selective rf pulse. It is shown that for the situation where the centre line is initially saturated, the satellite population follows a power law dependence that can be approximated by $C_1(L/a)^p(1/W_{dd})^{p/2}(t)^{p/2}$ for times greater than the domain-diffusion time $L^2/W_{dd}a^2$, where L,a and W_{dd} are the domain width, internuclear spacing and dipolar transition probability respectively. The results are quite general and are found in qualitative agreement with the ^{23}Na relaxation behaviour at low temperature in ferroelectric $NaNO_2$.

Keywords : Spin diffusion, domain wall effect in ferroelectrics, Spin lattice relaxation

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1. Introduction

Ferroelectrics are a very important class of materials having wide applications in various technological devices such as electro-optic materials, infrared sensors, ultrasonic systems *etc* [1-3]. A material is said to be ferroelectric when it has two or more orientational states of electric polarization and can be shifted from one to another of these states by an electric field. If the spontaneous polarization arises due to the ordering of ions or some group of ions, then the ferroelectric is termed as a order-disorder ferroelectric [1-3]. The thermal motions tend to destroy the ferroelectric order and ferroelectricity usually disappears above a certain temperature called the transition temperature T_C. Below T_C, a ferroelectric material comprises regions called domains within each of which the polarization is in the same direction but in the adjacent domains the polarization is in different direction. If the spontaneous polarization in the adjacent domains are in opposite directions, the domains are called 180° domains and the regions joining two adjacent domains are called 180° domain-walls. The technological applications of a ferroelectric greatly depend upon its domain-structure and behaviour and shape of hysteresis loop that in turn are governed by how fast the domains can be switched from one direction to the other. The switching process involves building up of the favourable domains at the expense of the unfavourable ones starting from nucleation and growth at the domain-walls [2]. Also, the properties of a ferroelectric tend to change over period of time due to gradual build up of inhibiting structure at domain-walls reducing their mobility [1,2]. Therefore, study of ferroelectric domains and domain walls has been drawing considerable attention of research workers in the past as well as recent years [4-10]. For this various techniques [1] such as optical birefringence, second harmonic generation, electron microscopy, chemical etching, X-ray topography, U. V. photoemission *etc.* have been used for different materials. Nuclear magnetic resonance (NMR) has been a very powerful tool for studying the local environment [11-13].

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Nuclei with spin quantum numbers $I \geq 1$ possess electric quadrupole moments in addition to the magnetic dipole moments. The dipole moments interact with the local magnetic field whereas the electric quadrupole moments interact with the electric field gradients. The NMR studies of nuclei with $I \geq 1$ have therefore proved to be a very powerful tool for the study of local structure and dynamics including phase transitions. A large number of reports are available on successful use of NMR for such investigations in ferroelectrics, a few illustrative ones are given in the references [14-17]. However, the possible effect of domain-walls on the spin relaxation has not been studied so far in literature for any ferroelectric system. In this paper, we present a theoretical study of the nuclear spin relaxation of spin $I = 3/2$ system due to domain-walls in order-disorder ferroelectrics. The formation of rate equations and their solutions are given in the next section, followed by the application of the results in interpretation of the experimental data in ferroelectric $NaNO_2$. A preliminary report of this work was presented earlier [18].

2. Theory

Let us consider a ferroelectric material of order-disorder type possessing $I = 3/2$ nuclei such as ^{23}Na in $NaNO_2$. We assume that a 180^0 domain can be represented by a one-dimensional array of equidistant nuclei (spin $I = 3/2$) situated at ... x-2a, x-a, x, x+a, x+2a ... as shown in Figure 1. In an external magnetic field, the $I = 3/2$ spins would have four Zeeman levels [12,13] corresponding to the quantum numbers $m = 3/2, 1/2, -1/2, -3/2$. We assume that the quadrupole-coupling constant is such that it gives rise to well resolved NMR spectrum corresponding to the centre line ($1/2 \leftrightarrow -1/2$) and satellite transitions ($\pm 3/2 \leftrightarrow \pm 1/2$).

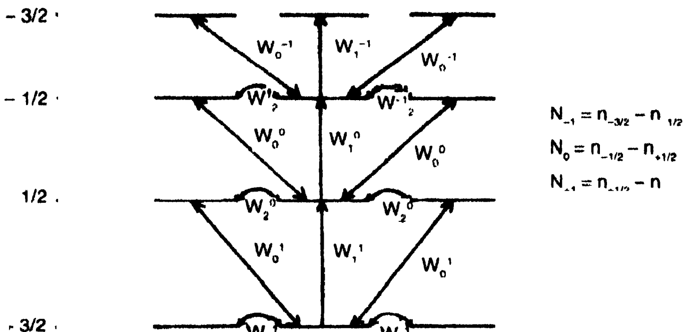

Figure 1. Schematic energy level diagram of spins (I=3/2) in a one dimensional chain. W^1_0, W^0_0, W^{-1}_0 are the transition probabilities of $3/2 \leftrightarrow 1/2$, $1/2 \leftrightarrow -1/2$, $-1/2 \leftrightarrow -3/2$ levels respectively for the case where one spin undergoing an upward transitions while the other spin undergoes downward transition (usually called flip-flop term). W^1_2, W^0_2, W^{-1}_2 represents simultaneous upward (or downward) flip of the pair of spins, W^1_1, W^0_1, W^{-1}_1 represents the single spin transition probability for the spin-pairs and counted twice for each pair of spins.

The rate of change of deviations of populations from thermal equilibrium values can be written as [12,13,19,20]

$$\frac{\partial n_{3/2}(x,t)}{\partial t} = -2n_{3/2}(x,t)\,W_1^1 + 2n_{1/2}(x,t)\,W_1^1$$

$$-\frac{1}{N} n_{3/2}(x,t)n_{1/2}(x+a,t)W_0^1 + \frac{1}{N} n_{1/2}(x,t)n_{3/2}(x+a,t)W_0^1$$

$$-\frac{1}{N} n_{3/2}(x,t)n_{1/2}(x-a,t)W_0^1 + \frac{1}{N} n_{1/2}(x,t)n_{3/2}(x-a,t)W_0^1$$

$$-\frac{1}{N} n_{3/2}(x,t)n_{3/2}(x+a,t)W_2^1 + \frac{1}{N} n_{1/2}(x,t)n_{1/2}(x+a,t)W_2^1$$

$$-\frac{1}{N} n_{3/2}(x,t)n_{3/2}(x-a,t)W_2^1 + \frac{1}{N} n_{1/2}(x,t)n_{1/2}(x-a,t)W_2^1$$

$$\frac{\partial n_{1/2}(x,t)}{\partial t} = 2n_{3/2}(x,t)\,W_1^1 - 2n_{1/2}(x,t)\,W_1^1$$

$$-2n_{1/2}(x,t)\,W_1^0 + 2n_{\ 1/2}(x,t)\,W_1^0 - \frac{1}{N} n_{3/2}(x-a,t)n_{1/2}(x,t)W_0^1$$

$$-\frac{1}{N} n_{1/2}(x,t)n_{3/2}(x+a,t)W_0^1 + \frac{1}{N} n_{3/2}(x,t)n_{1/2}(x-a,t)W_0^1$$

$$+\frac{1}{N} n_{3/2}(x,t)n_{1/2}(x+a,t)W_0^1 + \frac{1}{N} n_{\ 1/2}(x,t)n_{1/2}(x+a,t)W_0^0$$

$$-\frac{1}{N} n_{1/2}(x,t)n_{\ 1/2}(x-a,t)W_0^0 + \frac{1}{N} n_{-1/2}(x,t)n_{1/2}(x-a,t)W_0^0$$

$$-\frac{1}{N} n_{1/2}(x,t)n_{-1/2}(x+a,t)W_0^0 + \frac{1}{N} n_{3/2}(x,t)n_{3/2}(x+a,t)W_2^1$$

$$-\frac{1}{N} n_{1/2}(x,t)n_{1/2}(x+a,t)W_2^1 + \frac{1}{N} n_{3/2}(x,t)n_{3/2}(x-a,t)W_2^1$$

$$-\frac{1}{N} n_{1/2}(x,t)n_{1/2}(x-a,t)W_2^1 - \frac{1}{N} n_{1/2}(x,t)n_{1/2}(x+a,t)W_2^0$$

$$+\frac{1}{N} n_{-1/2}(x,t)n_{-1/2}(x+a,t)W_2^0 - \frac{1}{N} n_{1/2}(x,t)n_{1/2}(x-a,t)W_2^0$$

$$+\frac{1}{N} n_{-1/2}(x,t)n_{-1/2}(x-a,t)W_2^0\,.$$

$$\frac{\partial n_{-1/2}(x,t)}{\partial t} = 2n_{1/2}(x,t)\,W_1^0 - 2n_{-1/2}(x,t)\,W_1^0$$

$$-2n_{-1/2}(x,t)W_1^{-1} + 2n_{-3/2}(x,t)\,W_1^{-1} - \frac{1}{N} n_{1/2}(x-a,t)n_{-1/2}(x,t)W_0^0$$

$$-\frac{1}{N} n_{-1/2}(x,t)n_{1/2}(x+a,t)W_0^0 + \frac{1}{N} n_{1/2}(x,t)n_{-1/2}(x-a,t)W_0^0$$

$$+\frac{1}{N} n_{1/2}(x,t)n_{-1/2}(x+a,t)W_0^0 + \frac{1}{N} n_{-3/2}(x,t)n_{-1/2}(x+a,t)W_0^{-1}$$

$$-\frac{1}{N} n_{1/2}(x,t) n_{-3/2}(x-a,t) W_0^{-1} + \frac{1}{N} n_{-3/2}(x,t) n_{-1/2}(x-a,t) W_0^{-1}$$

$$\frac{1}{N} n_{1/2}(x,t) n_{-3/2}(x+a,t) W_0^{-1} + \frac{1}{N} n_{1/2}(x,t) n_{1/2}(x+a,t) W_2^{0}$$

$$-\frac{1}{N} n_{1/2}(x,t) n_{-1/2}(x+a,t) W_2^{0} + \frac{1}{N} n_{1/2}(x,t) n_{1/2}(x-a,t) W_2^{0}$$

$$-\frac{1}{N} n_{-1/2}(x,t) n_{-1/2}(x-a,t) W_2^{0} - \frac{1}{N} n_{-1/2}(x,t) n_{-1/2}(x+a,t) W_2^{-1}$$

$$+\frac{1}{N} n_{-3/2}(x,t) n_{-3/2}(x+a,t) W_2^{-1} - \frac{1}{N} n_{-1/2}(x,t) n_{-1/2}(x-a,t) W_2^{-1}$$

$$+\frac{1}{N} n_{3/2}(x,t) n_{-3/2}(x-a,t) W_2^{-1},$$

$$\frac{\partial n_{-3/2}(x,t)}{\partial t} = 2n_{-1/2}(x,t) W_1^{-1} - 2n_{-3/2}(x,t) W_1^{-1}$$

$$+\frac{1}{N} n_{-1/2}(x,t) n_{-3/2}(x+a,t) W_0^{-1} - \frac{1}{N} n_{-3/2}(x,t) n_{-1/2}(x+a,t) W_0^{-1}$$

$$+\frac{1}{N} n_{1/2}(x,t) n_{-3/2}(x-a,t) W_0^{-1} - \frac{1}{N} n_{-3/2}(x,t) n_{-1/2}(x-a,t) W_0^{-1}$$

$$+\frac{1}{N} n_{-1/2}(x,t) n_{-1/2}(x+a,t) W_2^{-1} - \frac{1}{N} n_{-3/2}(x,t) n_{-3/2}(x+a,t) W_2^{-1}$$

$$+\frac{1}{N} n_{-1/2}(x,t) n_{-1/2}(x-a,t) W_2^{-1} - \frac{1}{N} n_{-3/2}(x,t) n_{-3/2}(x-a,t) W_2^{-1}, \tag{1}$$

where $N = n_{3/2} + n_{1/2} + n_{-1/2} + n_{-3/2}$

and W_0^1, W_0^0, W_0^{-1} are the transition probabilities of $3/2 \leftrightarrow 1/2$, $1/2 \leftrightarrow -1/2$, $-1/2 \leftrightarrow -3/2$ levels respectively for the case where one spin undergoing an upward transitions while the other spin undergoes downward transition (usually called flip-flop term). W^1_2, W^0_2, W^{-1}_2 represent simultaneous upward (or downward) flip of the pair of spins, W^1_1, W^0_1, W^{-1}_1 represent the single spin transition probability for the spin-pairs and counted twice for each pair of spins.

Defining

$$N_{+1} = n_{3/2} - n_{1/2},$$

$$N_0 = n_{+1/2} - n_{-1/2},$$

$$N_{-1} = n_{-1/2} - n_{-3/2},$$

and assuming that

$$W^i_0 = W^i_0(x, x+a) \cong W^i_0(x, x-a) \qquad (\text{for } i = 1, 0, -1)$$

and $\quad W^i_2 = W^i_2(x, x+a) \cong W^i_2(x, x-a),$

We can write eq. (1) as

$$\frac{\partial N_{+1}}{\partial t}(x,t) = -2\rho N_{+1}(x,t) - 2\sigma N_{+1}(x+a,t) - 2\sigma N_{+1}(x-a,t)$$
$$+\rho' N_0(x,t) + \sigma' N_0(x+a,t) + \sigma' N_0(x-a,t),$$

$$\frac{\partial N_0}{\partial t}(x,t) = \rho N_{+1}(x,t) + \sigma N_{+1}(x+a,t) + \sigma N_{+1}(x-a,t)$$
$$-2\rho' N_0(x,t) - 2\sigma' N_0(x+a,t) - 2\sigma' N_0(x-a,t)$$
$$+\rho'' N_{-1}(x,t) + \sigma'' N_{-1}(x+a,t) + \sigma'' N_{-1}(x-a,t),$$

$$\frac{\partial N_{-1}}{\partial t}(x,t) = \rho' N_0(x,t) + \sigma' N_0(x+a,t) + \sigma' N_0(x-a,t)$$
$$-2\rho'' N_{-1}(x,t) - 2\sigma'' N_{-1}(x+a,t) - 2\sigma'' N_{-1}(x-a,t),$$

where $\rho = 2W_1^1 + (W_0^1/2) + (W_2^1/2)$, $\sigma = (W_2^1 - W_0^1)/4$

$$\rho' = 2W_1^0 + (W_0^0/2) + (W_2^0/2),\ \sigma' = (W_2^0 - W_0^0)/4$$

$$\rho'' = 2W_1^{-1} + (W_0^{-1}/2) + (W_2^{-1}/2),\ \sigma'' = (W_2^{-1} - W_0^{-1})/4. \tag{2}$$

Using Taylor series expansion of the terms $N_{+1}(x+a, t)$, $N_{-1}(x+a, t)$, $N_0(x+a, t)$, $N_0(x-a, t)$, $N_{-1}(x-a, t)$, $N_{+1}(x-a, t)$, and retaining the terms up to the second derivative and taking

$$\rho + 2\sigma = a_1,\ \rho' + 2\sigma' = a_2,\ \rho'' + 2\sigma'' = a_3,$$

$$D_1 = -\sigma a^2,\ D_2 = -\sigma' a^2,\ D_3 = -\sigma'' a^2,$$

the eq. (2) reduces to

$$\frac{\partial N_{+1}}{\partial t}(x,t) = -2a_1 N_{+1}(x,t) + 2D_1 \frac{\partial^2}{\partial x^2} N_{+1}(x,t)$$
$$+a_2 N_0(x,t) - D_2 \frac{\partial^2}{\partial x^2} N_0(x,t),$$

$$\frac{\partial N_0}{\partial t}(x,t) = a_1 N_{+1}(x,t) - D_1 \frac{\partial^2}{\partial x^2} N_{+1}(x,t) - 2a_2 N_0(x,t)$$
$$+2D_2 \frac{\partial^2}{\partial x^2} N_0(x,t) + a_3 N_{-1}(x,t) - D_3 \frac{\partial^2}{\partial x^2} N_{-1}(x,t),$$

$$\frac{\partial N_{-1}}{\partial t}(x,t) = a_2 N_0(x,t) - D_2 \frac{\partial^2}{\partial x^2} N_0(x,t) - 2a_3 N_{-1}(x,t)$$
$$+2D_3 \frac{\partial^2}{\partial x^2} N_{-1}(x,t). \tag{3}$$

Now we attempt to solve these coupled simultaneous differential equation using Laplace transform [21, 22]. Taking the Laplace transform of eq. (3) over the variable t and writing

$$Z_{+1} = \mathcal{L}\{N_{+1}(x,t)\}, Z_0 = \mathcal{L}\{N_0(x,t), Z_{-1} = \mathcal{L}\{N_{-1}(x,t)\},$$

we get

$$4C_2\frac{\partial^2 Z_{+1}}{\partial x^2}+(4C_1+3s)\,Z_{+1}+2sZ_0+sZ_{-1}=k_1$$

$$2C_4\frac{\partial^2 Z_0}{\partial x^2}+s\,Z_{+1}+(2s+2C_3)\,Z_0+sZ_{-1}=k_2\,, \qquad (4)$$

$$4C_6\frac{\partial^2 Z_{-1}}{\partial x^2}+s\,Z_{+1}+2sZ_0+(4C_5+3s)\,Z_{-1}=k_3\,.$$

with

$$k_1=3\,N_{+1}(x,0)+N_{-1}(x,0)+2N_0(x,0),$$

$$k_2=N_{+1}(x,0)+N_{-1}(x,0)+2N_0(x,0),$$

$$k_3=N_{+1}(x,0)+3N_{-1}(x,0)+2N_0(x,0),$$

and

$$C_1=2W_1^1+W_2^1\,, \qquad C_2=-\frac{a^2}{4}\left(W_0^1-W_2^1\right),$$

$$C_3=2W_1^0+W_2^0\,, \qquad C_4=-\frac{a^2}{4}\left(W_0^0-W_2^0\right),$$

$$C_5=2W_1^{-1}+W_2^{-1}\,, \qquad C_6=-\frac{a^2}{4}\left(W_0^{-1}-W_2^{-1}\right).$$

For the given $I = 3/2$ system, the value of the probabilities can be written as [13]

$$W_0^1=\frac{9}{8}\frac{A_0^2}{\hbar^2}\left(1-3\cos^2\theta\right)^2\tau_c\,,$$

$$W_1^1=\frac{27}{8}\frac{A_0^2}{\hbar^2}\sin^2\theta\cos^2\theta\,\tau_c\,,$$

$$W_0^0=2\frac{A_0^2}{\hbar^2}\left(1-3\cos^2\theta\right)^2\tau_c\,,$$

$$W_1^0=\frac{9}{8}\frac{A_0^2}{\hbar^2}\sin^2\theta\cos^2\theta\,\tau_c\,,$$

$$W_r^{-1}=\frac{9}{8}\frac{A_0^2}{\hbar^2}\left(1-3\cos^2\theta\right)^2\tau_c$$

$$W_1^{-1}=\frac{243}{8}\frac{A_0^2}{\hbar^2}\sin^2\theta\cos^2\theta\,\tau_c$$

$$W_2^1=\frac{81}{8}\frac{A_0^2}{\hbar^2}\sin^4\theta\,\tau_c$$

$$W_2^0=18\frac{A_0^2}{\hbar^2}\sin^4\theta\,\tau_c\,,$$

$$W_2^{-1}=\frac{81}{8}\frac{A_0^2}{\hbar^2}\sin^4\theta\,\tau_c\,,$$

where $A_0=\gamma_I\cdot\gamma_I\,\hbar^2/r^3$, θ is the polar angle of the radiu vector joining two nuclei with respect to the external magneti field and, τ_c is the correlation time.

The eq.(4) were difficult to solve for the general case. So w made a simplifying assumption that the direction of the extern static magnetic field H_0 used in a NMR experiment is at rigl angles to the array of spins, so that θ is equal to 90°. We furth assume that there is no cross-relaxation between the satelli and centre line transitions. We therefore set C_1, C_3 and C_5 equ to zero. The eq.(4) then reduces to

$$Z''_{+1}=-\frac{1}{9|b|}\left[k_1-3s\,Z_{+1}-2s\,Z_0-s\,Z_{-1}\right],$$

$$Z''_0=\frac{1}{8|b|}\left[k_2-s\,Z_{+1}-2s\,Z_0-s\,Z_{-1}\right],$$

$$Z''_{-1}=-\frac{1}{9|b|}\left[k_3-s\,Z_{+1}-2s\,Z_0-3s\,Z_{-1}\right],$$

where $|b|=a^2W_{00}/16$, $W_{00}=W_0^0=(2A_0^2/\hbar^2)(1-3\cos$ τ_c and s is the Laplace variable (see Appendix-I).

The set of eqs. (5) can be solved for different initial a boundary conditions. For an easy comparison of the resul with the generally performed pulsed NMR relaxati measurements and also to study the domain-wall effects, v consider the following situations.

A selective radio frequency NMR pulse is applied to t centre line of the quadrupole split well resolved spectrum of I 3/2 system for a duration such that a fraction α of spins flip fro the lower state $I = 1/2$ to the higher state $I = -1/2$ and t population difference become

$$N_0(x,0)=-2\alpha\,,\quad N_{-1}(x,0)=\alpha\,,\quad N_{+1}(x,0)=\alpha\,. \qquad ($$

The time $t = 0$ corresponds to the end of the pulse. V consider a 180° domain with the domain-wall at its end. Tl origin of the coordinates $x = 0$, is taken at the domain-wall. V further assume that the populations at the domain-wall follo the time dependence

$$N_{\pm1}(0,t)=\alpha\,e^{-2W_1t}$$

$$N_0(0,t)=\alpha\left[e^{-2W_1t}+e^{-2W_2t}\right], \qquad ($$

where W_1 and W_2 are the quadrupolar relaxation probabilit corresponding to the transition $m = \pm 3/2 \leftrightarrow \pm 1/2$ ar $m = \pm 3/2 \leftrightarrow \mp 1/2$ respectively. The significance of this particul choice would become clear when we discuss the results NaNO$_2$ later on. It should be noted in deciding the location the origin, *i.e.* $x = 0$, that the NMR of nuclei lying inside the w would not be usually observable due to structural disorders. So, $x = 0$ would correspond to the region near the wall. At present, we are assuming that the wall thickness is negligible.

Using the above boundary conditions, eq. (5) were solved to yield

$$N_{+1}(x,s) = -b_1(1-\varphi_1^2/18)\, e^{-m_1 x} - b_2(1-\varphi_2^2/18)\, e^{-m_2 x}$$

$$-(k_1 - k_3/4s)\, e^{-x\sqrt{\mu s}} + (2k_1 - 2k_2/4s),$$

$$N_0(x,s) = b_1 e^{-m_1 x} + b_2 e^{-m_2 x} - (k_1 - 4k_2 + k_3)/4s,$$

$$N_{-1}(x,s) = b_1(1-\varphi_1^2/18)\, e^{-m_1 x} - b_2(1-\varphi_2^2/18)\, e^{-m_2 x}$$

$$+(k_1 - k_3/4s)\, e^{-x\sqrt{\mu s}} + (2k_3 - 2k_2/4s), \qquad (8)$$

with

$$\varphi_1^2 = 25+\sqrt{337}, \quad \varphi_2^2 = 25-\sqrt{337},$$

$$m_1 = \varphi_1\sqrt{s}/\sqrt{72|b|}, \quad m_2 = \varphi_2\sqrt{s}/\sqrt{72|b|}, \quad \mu = 2/9|b|,$$

$$\frac{18}{\varphi_2^2-\varphi_1^2}\left\{\frac{k_1-2k_2+k_3}{4s} - \left(\frac{\varphi_1^2}{18}-1\right)\frac{k_1-4k_2+k_3}{4s}\right.$$

$$+\frac{\varphi_1^2}{18}\frac{\alpha}{s+2W_1} + \left(\frac{\varphi_1^2}{18}-1\right)\frac{\alpha}{s+2W_1} \quad \frac{k_1-4k_2+k_3}{4s}$$

$$\frac{\alpha}{s+2W_1} \quad \frac{\alpha}{s+2W_2},$$

$$\frac{18}{\varphi_2^2-\varphi_1^2}\left\{\frac{k_1-2k_2+k_3}{4s} - \left(\frac{\varphi_1^2}{18}-1\right)\frac{k_1-4k_2+k_3}{4s}\right.$$

$$\left.+\frac{\varphi_1^2}{18}\cdot\frac{\alpha}{s+2W_1} + \left(\frac{\varphi_1^2}{18}-1\right)\frac{\alpha}{s+2W_2}\right\}.$$

Taking inverse Laplace transform [22] of eq. (8), the values of $N_{\pm1}(x,t)$ and $N_0(x,t)$ are obtained as

$$N_{+1}(x,t) = C_{11}\,\phi_1(x,t) + C_{12}\,\phi_2(x,t) + C_{13}\,\phi_3(x,t) + C_{14}\,\phi_4(x,t)$$

$$+C_{15}\,\phi_5(x,t) + C_{16}\,\phi_6(x,t) + C_{17}\,\phi_7(x,t) + C_{18},$$

$$N_{-1}(x,t) = C_{21}\,\phi_1(x,t) + C_{22}\,\phi_2(x,t) + C_{23}\,\phi_3(x,t) + C_{24}\,\phi_4(x,t)$$

$$+C_{25}\,\phi_5(x,t) + C_{26}\,\phi_6(x,t) + C_{27}\,\phi_7(x,t) + C_{28},$$

$$N_0(x,t) = C_{31}\,\phi_1(x,t) + C_{32}\,\phi_2(x,t) + C_{33}\,\phi_3(x,t) + C_{34}\,\phi_4(x,t)$$

$$+C_{35}\,\phi_5(x,t) + C_{36}\,\phi_6(x,t) + C_{38}, \qquad (9)$$

where

$$C_{11} = C_{21} = -\left(1-\frac{\psi_1}{18}\right)C_{31}$$

$$\frac{\varphi_1^2}{18}\;\frac{\dfrac{(k_1-2k_2+k_3)}{\varphi_2^2-\varphi_1^2} + \dfrac{18}{\varphi_2^2-\varphi_1^2}\times\left(\dfrac{\varphi_1^2}{18}-1\right)}{(k_1-4k_2+k_3)\,,\;(k_1-4k_2+k_3)}$$

$$C_{12} = C_{22} = -\left(1-\frac{\varphi_1^2}{18}\right)C_{32} = \left(1-\frac{\varphi_1^2}{18}\right)\left(\frac{\varphi_2^2}{\varphi_2^2-\varphi_1^2}\right)$$

$$C_{13} = C_{23} = -\left(1-\frac{\varphi_1^2}{18}\right)C_{33} = \left(1-\frac{\varphi_1^2}{18}\right)\left(\frac{\varphi_1^2}{18}-1\right)\frac{18}{\varphi_2^2-\varphi_1^2}+1$$

$$C_{14} = C_{24} = -\left(1-\frac{\varphi_2^2}{18}\right)C_{34}$$

$$\frac{\varphi_2^2}{18}\;\frac{\dfrac{18}{4}\dfrac{(k_1-2k_2+k_3)}{\varphi_2^2-\varphi_1^2} - \dfrac{18}{\varphi_2^2-\varphi_1^2}\times}{\left(\dfrac{\varphi_1^2}{18}-1\right)\times\left((k_1-4k_2+k_3)\right)}$$

$$C_{15} = C_{25} = -\left(1-\frac{\varphi_2^2}{18}\right)C_{35} = -\left(1-\frac{\varphi_2^2}{18}\right)\left(\frac{\varphi_1^2}{\varphi_2^2-\varphi_1^2}\right)$$

$$C_{16} = C_{26} = -\left(1-\frac{\varphi_2^2}{18}\right)C_{36} = -\left(1-\frac{\varphi_2^2}{18} \quad \frac{\varphi_1^2}{18} \quad \right)\frac{18}{\varphi_2^2-\varphi_2^2}$$

$$C_{17} = -\frac{k_1-k_3}{4}, \quad C_{27} = \frac{k_1-k_3}{4}, \quad C_{18} = \frac{k_1-k_2}{2},$$

$$C_{28} = \frac{k_3-k_2}{2}, \quad C_{38} = \quad k_1-4k_2+k_3$$

with

$$\phi_1(x,t) = \mathrm{erfc}\left(\frac{x\varphi_1}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right),$$

$$\phi_2(x,t) = \frac{\alpha}{2}e^{-2W_1 t}\left[e^{-\sqrt{-2W_1}\frac{x\varphi_1}{\sqrt{72|b|}}}\,\mathrm{erfc}\left(-\sqrt{-2W_1 t} + \frac{x\varphi_1}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right) + e^{\sqrt{-2W_1}\frac{x\varphi_1}{\sqrt{72|b|}}}\,\mathrm{erfc}\left(\sqrt{-2W_1 t} + \frac{x\varphi_1}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right)\right]$$

$$\phi_3(x,t) = \frac{\alpha}{2}e^{-2W_2 t}\left[e^{-\sqrt{-2W_2}\frac{x\varphi_1}{\sqrt{72|b|}}}\,\mathrm{erfc}\left(-\sqrt{-2W_2 t} + \frac{x\varphi_1}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right) + e^{\sqrt{-2W_2}\frac{x\varphi_1}{\sqrt{72|b|}}}\,\mathrm{erfc}\left(\sqrt{-2W_2 t} + \frac{x\varphi_1}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right)\right)$$

$$\phi_4(x,t) = \mathrm{erfc}\left(\frac{x\varphi_2}{72|b|}\frac{1}{2\sqrt{t}}\right),$$

$$\phi_5(x,t) = \frac{\alpha}{2}e^{-2W_1 t}\left\{ e^{-\sqrt{-2W_1}\frac{x\varphi_2}{\sqrt{72|b|}}}\mathrm{erfc}\left(-\sqrt{-2W_1 t} + \frac{x\varphi_2}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right) + e^{\sqrt{-2W_1}\frac{x\varphi_2}{\sqrt{72|b|}}}\mathrm{erfc}\left(\sqrt{-2W_1 t} + \frac{x\varphi_2}{\sqrt{72|b|}\,2\sqrt{t}}\right)\right\}$$

$$\phi_6(x,t) = \frac{\alpha}{2}e^{-2W_2 t}\left\{ e^{-\sqrt{-2W_2}\frac{x\varphi_2}{\sqrt{72|b|}}}\mathrm{erfc}\left(-\sqrt{-2W_2 t} + \frac{x\varphi_2}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right) + e^{\sqrt{-2W_2}\frac{x\varphi_2}{\sqrt{72|b|}}}\mathrm{erfc}\left(\sqrt{-2W_2 t} + \frac{x\varphi_2}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right)\right\}$$

$$\phi_7(x,t) = \mathrm{erfc}\left(x\sqrt{\frac{2}{9|b|}}\,\frac{1}{2\sqrt{t}}\right),$$

where erfc is the complementary error function (see Appendix–I)

The average values of the population differences for the entire domain would be given by

$$N_i(t) = (1/L)\int^{L} N_i(x,t)\,dx, \tag{10}$$

where $i = 1, 0$ or -1 and L is the thickness of the domain. In our treatment domain-wall thickness has been ignored.

3. Result and discussion

The time dependence of the population difference $N_{+1}(t)$, $N_{-1}(t)$ and $N_0(t)$ were evaluated numerically using eqs.(9) and (10) for different values of the ratios W_1/W_{00} and W_2/W_1 and are plotted in Figure 2. It was found that the values of W_2/W_1 in the range 0.5 to 2.0 which are typical for ferroelectrics such as $NaNO_2$ does not affect the population difference much [23]. Therefore the population difference is plotted for only one ratio of W_2/W_1 viz. $W_2/W_1 = 1$. The curves shown by dotted line depict the behaviour given by eq. (7) *i.e.* they show the time dependence of $N_{\pm 1}(t)$, where the nuclei at all the sites x through-out the domain follow the relation given by eq.(7) and spin-diffusion absent. From the Figure 2(b), it is seen that $N_{\pm 1}(t)$ for the present situation are non exponential.

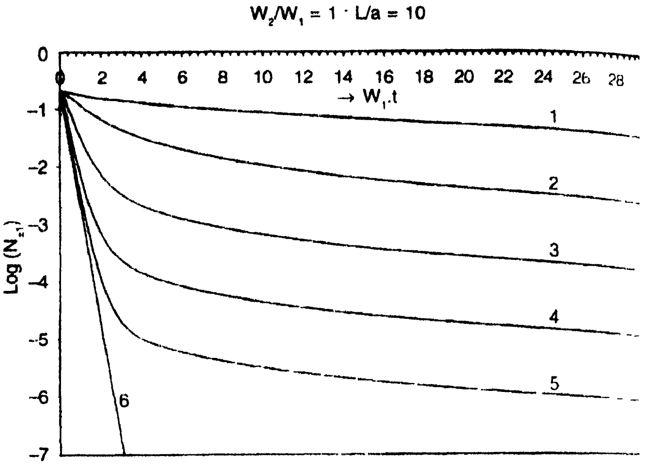

Figure 2(b). Variation of $\mathrm{Log}_e\ N_{\pm 1}(t)$ as a function of $W_1 t$ for different ratios of W_1/W_{00}

If we treat the quantity $W_{00}a^2$ as the diffusion coefficient [12], then the function $\sqrt{W_{00}a^2 t}$ becomes the diffusion length and provides an estimate of the distance upto which the magnetization would have diffused from the domain-wall ($x = 0$) into the domain in time t. The quantity $L/\sqrt{W_{00}a^2 t}$ then gives an estimate of the portion of the domain of length L getting affected in time t. The spin-diffusion would have travelled the full domain in a time t_1 where $\sqrt{W_{00}t_1} = L/a$. Figure 3 shows a plot of $\log_e N_{\pm 1}(t)$ *vs* $\log_e(\sqrt{W_{00}t}\ /\ L/a)$. From the Figure 3,

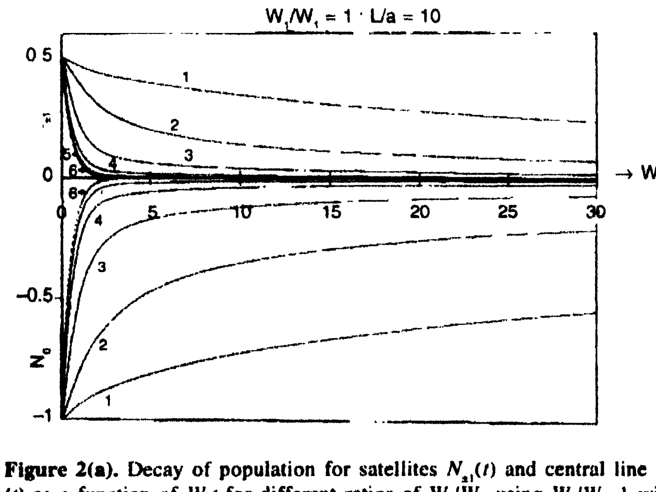

Figure 2(a). Decay of population for satellites $N_{\pm 1}(t)$ and central line $N_0(t)$ as a function of $W_1 t$ for different ratios of W_1/W_{00} using $W_2/W_1 = 1$ with curve no. 1, 2, 3, 4, 5 represent $W_1/W_{00} =$ 1, 0.1, 0.01, 0.001, 0.0001 respectively, and curve 6 represents the behaviour given by Eq. (7).

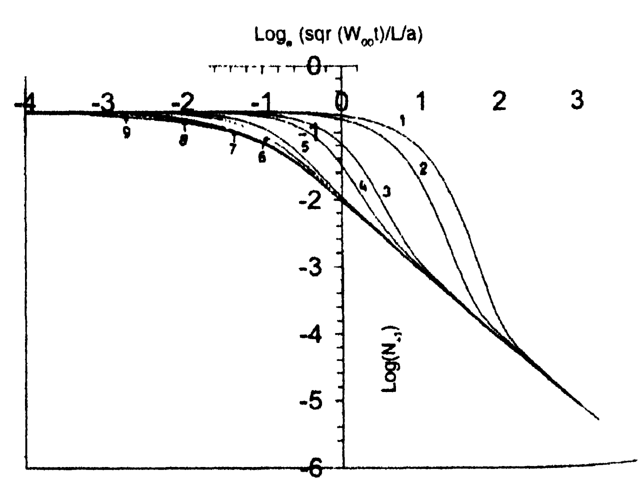

Figure 3. Variation of $\mathrm{Log}_e\ N_{\pm 1}(t)$ as a function of $\mathrm{Log}_e[(\sqrt{W_{00}t})/(L/a)]$ for different W_1/W_{00} ratio. Curve 1 through 9 represent $W_1/W_{00} =$ 0.0001, 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, 1, 10 respectively.

find that for the values of $\log_e (\sqrt{W_{00}t} / L/a) \geq 1$ *i.e.* $\sqrt{W_{00}a^2 t} > L$, $N_{\pm1}(t)$ follows the relation $N_{\pm1}(t) = C_1(L/a)^p (1/W_{00})^{p/2} t^{-p/2}$. The values of C_1 and p would depend upon the ratios W_2/W_1 and W_1/W_{00}. We get $p = 1.03$ and $C_1 = \exp(-2)$ for $W_2/W_1 = 1$ and $W_1/W_{00} = 1$. For the $L/\sqrt{W_{00}a^2}$, the effect of domain-wall would not be visible, and for times much greater than $L/\sqrt{W_{00}a^2}$, the population differences follow the power law dependence $t^{-p/2}$. For the time t in the range $(.05L)^2/(W_{00}a^2) < t < (L^2/W_{00}a^2)$, $N_{\pm1}(t)$ follows the curved portion in Figure 3. It was found that the behaviour of $N_{\pm1}(t)$ which is governed by eq.(10) may be crudely expressed by the empirical relation

$$N_{\pm1}(t) = \frac{N_{\pm1}(0)}{\left[1 + d\left(\frac{\sqrt{W_{00}t}}{L/a}\right)^p\right]}, \tag{11}$$

where p and d depend upon the ratio W_1/W_{00}. Their values were found not to vary significantly with the ratio W_2/W_1 and lie in the range 1 to 3 and 0.4 to 3 respectively. For example, $d = 3.68$, $p = 1.03$ for $W_1/W_{00} = 1$. The eq. (11) represents the time dependence of the magnetization corresponding to the transition $\pm 3/2 \leftrightarrow \pm 1/2$ as the magnetization would be proportional to $N_{\pm1}(t)$.

The value of $N_{\pm1}(0)/e \approx 0.184$ lies in the curved portions in Figure 3. If we assume that the time when the magnetization corresponding to the transition $\pm 3/2 \leftrightarrow \pm 1/2$ has decayed to $1/e$ of the initial value $N_{\pm1}(0)$, can be taken as a sort of measure for the relaxation time, we find that, the relaxation time, say T_{1dw}, due to domain-wall effect comes to be equal to

$$T_{1dw} = \frac{1}{W_{00}} \frac{\left(\frac{L}{a}\right)^2}{\left(\frac{d}{e-1}\right)^{\frac{2}{p}}}. \tag{12}$$

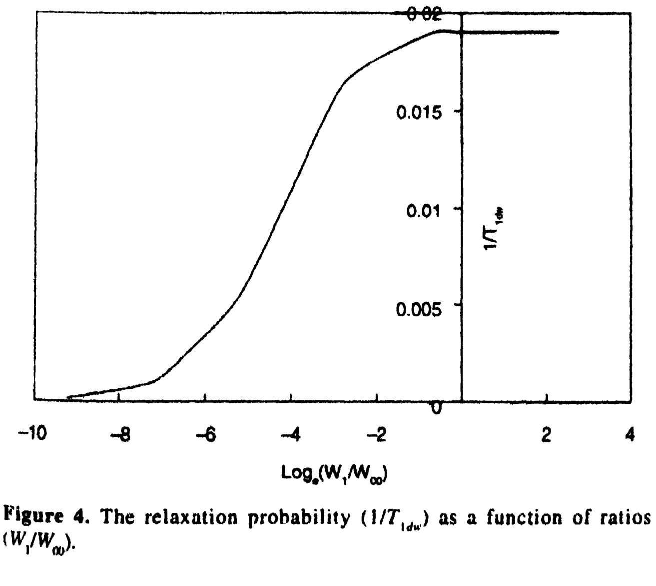

Figure 4. The relaxation probability ($1/T_{1dw}$) as a function of ratios (W_1/W_{00}).

The relaxation probability ($1/T_{1dw}$) due to spin-diffusion is plotted as a function of different values of W_1/W_{00} in Figure 4. It is clear from Figure 4 that $1/T_{1dw}$ is very small and almost independent of W_1/W_{00} for low values of W_1/W_{00}, and rises very fast as W_1/W_{00} increases and reaches almost a constant value for large values of W_1/W_{00}. Similar treatment may be presented for the behaviour of $N_0(t)$.

4. Explanation of the ^{23}Na spin-lattice relaxation data in ferroelectric $NaNO_2$.

Sodium nitrite is an order-disorder ferroelectric [24] with the ferroelectric to paraelectric transition temperature T_C at 438K[25,26]. The NMR studies have been carried out for different crystal orientation over the temperature range 130K to 462K [27] and it has been shown that the NO_2 groups have a spiral orientation as one moves from one 180^0 domain to the other and the domain-walls have structure like Bloch walls [28]. The crystal structure and the domain configuration for ferroelectric $NaNO_2$ are shown in Figure 5 and 6. The spin-lattice relaxation studies of ^{23}Na spins have been extensively carried out by Hughes and coworkers as a function of temperature and crystal orientation. The relaxation rate of ^{23}Na spins as function of temperature is shown in Figure 7. Figure 7 shows the available experimental data [29] of the relaxation probability, W_{sat}, of the upper satellite of ^{23}Na nuclei, which was measured by saturating the central resonance by a selective pulse and monitoring the time dependence of the satellite signal. The external field H_0 was parallel to the crystal symmetry axis so that the 180^0 domains are stacked at right angles to H_0. In Figure 7, are also shown the values of $W_{eff} = W_{sat} - W_{lph} - W_{mag}$ obtained after subtracting the contributions due to phonon W_{1ph} and magnetic relaxation process W_{mag} which occur at very low temperatures. It has been established by Pandey and Hughes [29] that the spin-lattice relaxation in the temperature range 437K (T_c) to 230K is quadrupolar and is caused by the flipping NO_2 groups. It has been further shown that the relaxation is magnetic at temperatures around 130K[30]. The relaxation behaviour in the temperature range 230K to about 170K could not be explained by the model involving the flipping motion of NO_2 groups and no explanation seems to have been presented so far. In what follows we make

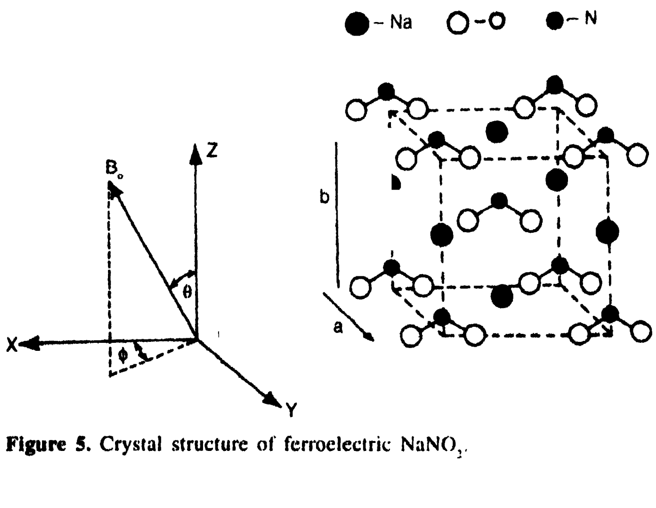

Figure 5. Crystal structure of ferroelectric $NaNO_2$.

an attempt to explain the low temperature behaviour of ^{23}Na satellite relaxation in $NaNO_2$ at temperature below 230K shown by the dotted curve of Figure 7.

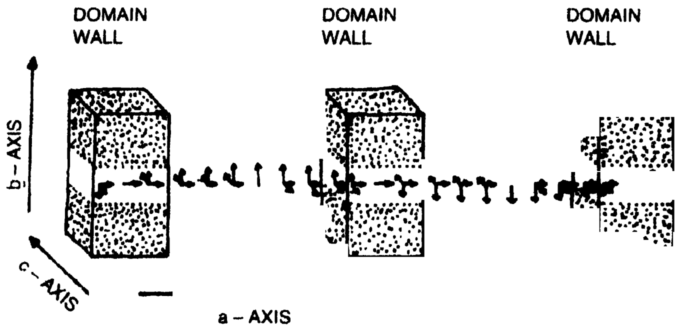

Figure 6. Spiraxlling local electric polarization in multi-domain crystal of $NaNO_2$.

The $NaNO_2$ crystal consists of 180^0 domains and the NO_2 groups giving rise to the spontaneous polarization have a spiral orientation [28] as shown in Figure 6. The polarization undergoes a reorientation from one domain to the other and would do more severely so near the domain-walls. If we visualize the whole sample to be made up of thin slices, than it means that the polarization in neighboring slices in the larger body of the domain are almost parallel to each other whereas the polarization in the slices close to the wall have progressive relative tills. As a result the activation barrier Ea for the flipping motion of the NO_2 groups in the region close to the domain-wall would be lower as

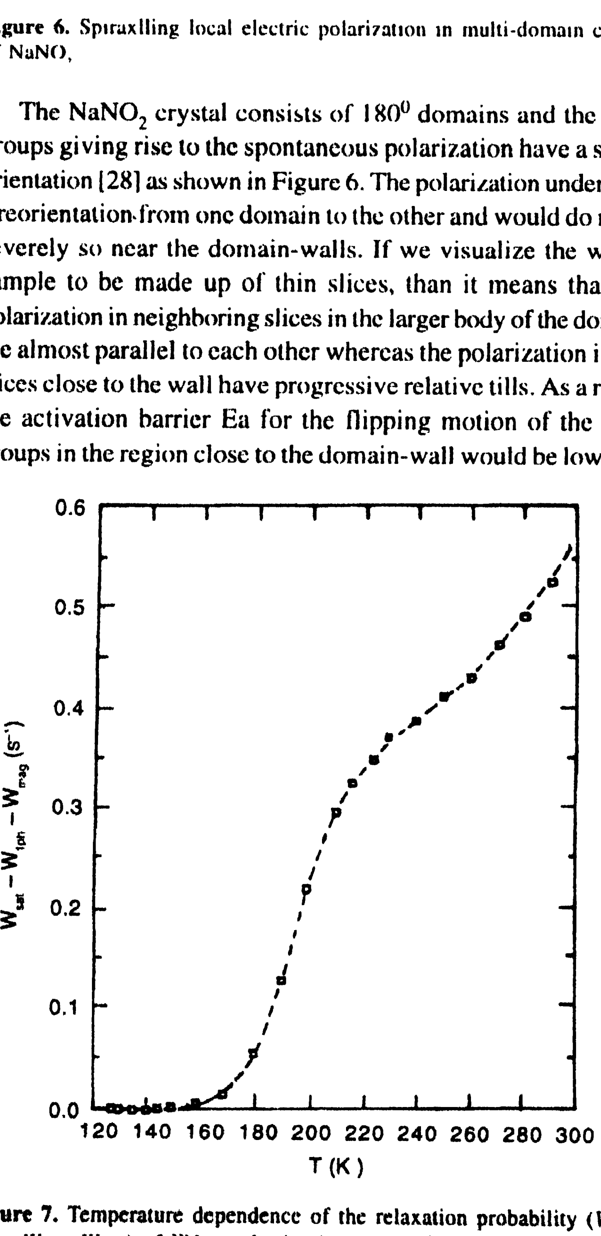

Figure 7. Temperature dependence of the relaxation probability ($W_{eff} = W_{sat} - W_{1ph} - W_{mag}$) of ^{23}Na nuclei in single crystal of $NaNO_2$ for satellite transition. W_{1ph} and W_{mag} represent the contribution due to phonon and magnetic relaxation process. □ - Experimental values. --- line drawn for a guide to the eye.

compared to that for the region deep inside the domain. By considering the flip probability to vary as [1] $e^{-Ea/kT}$, this implies that at lower temperatures when the flips of NO_2 groups in the interior body of the domain would have almost ceased, the groups near or inside the wall may still be executing some flipping motions. This, in turn, would cause the ^{23}Na ($I = 3/2$) spins near the wall to relax due of fluctuating electric field gradients [13]. Thus, we may assume that the ^{23}Na spins near the wall are relaxing though quadrupolar relaxation process [13] with transition probabilities W_1 and W_2 between $m = \pm 3/2 \leftrightarrow \pm 1/2$ and $m = \pm 3/2 \leftrightarrow \mp 1/2$ respectively [26,28]. If we assume that at low temperatures, other relaxation processes, except spin diffusion from domain-walls, have ceased, then we can directly apply the theory developed in Sections 2 and 3.

As discussed in Section 4, the magnetization corresponding to the satellite transition $m = \pm 3/2 \leftrightarrow \pm 1/2$, which is proportional to the population difference $N_{\pm 1}(t)$ various approximately according to the expression given in eq. (11) and a relaxation time due to spin diffusion from domain-walls can be given by eq. (12). The temperature dependence of the relaxation time would come from the temperature dependence of W_1, W_2, W_{00} and a. It was observed in Section 3, that the relaxation rate $1/T_{1dw}$, due to domain-walls does not significantly depend upon the ratio W_2/W_1. Therefore, the temperature dependence of $1/T_{1dw}$ would come from the temperature dependence of W_1/W_{00} and a. At lower temperatures, the lattice constants for $NaNO_2$ do not vary much [31]; therefore, W_{00} also would not vary so much as it is a function of a. Also, as the temperature decreases, W_1 being caused by the flipping NO_2 groups at domain walls decreases, and hence the ratio W_1/W_{00} also decreases. Now, a quick look at the Figure 4 reveals that for values of W_1/W_{00} greater than 0.5, $1/T_{1dw}$ is almost constant and decreases very fast as W_1/W_{00} decreases, finally, attaining almost a fixed value at very low values of W_1/W_{00}, we see that this is what is observed experimentally for $NaNO_2$ as shown in Figure 7. The Figure 7 shows that around 230K, the curve slightly flattens, then shows a steep fall and further becoming flat at low temperatures. The flattening of the curve around 230K indicates that W_1/W_{00} is larger than 0.5. The sharp increasing slope in Figure 7 above 230K indicates that the quadrupolar relaxation process takes over very fast at higher temperatures. Thus, our theory qualitatively explains the low temperature relaxation behaviour of ^{23}Na satellite in ferroelectric $NaNO_2$. Also, it suggests that the domain walls do have a non-negligible contribution in the spin relaxation process and in general, the overall relaxation rate, which is the sum of the relaxation rates due to various processes, would contain a term corresponding to this. Work on a quantitative analysis and solving eq. (4) for general orientation of the magnetic field is in progress and would be published elsewhere. We believe that this is probably the first report of study of the effect of domain walls on spin lattice relaxation in ferroelectrics.

It is to be mentioned here that the treatment presented so far deals with the changes produced in spin populations due to relaxation effect caused by thermally fluctuating (flipping) electric dipoles. This change has been further used to estimate the over-all relaxation time of $I = 3/2$ spins in order-disorder ferroelectrics. The experimental measurements of spin-lattice relaxation times essentially involve applications of intense radio-frequency pulses and monitoring the evolution of magnetization with time. If the sample has permanent electric dipole moment as is the case with ferroelectrics, another contribution arising due to the interaction of electric dipole moments with the rf pulse would also be present. This, so called piezoelectric contribution, sometimes is so large that it is impossible to see the free induction decay signal after the rf pulse. Methods have been devised by Hughes and Pandey [32] to overcome this problem in NMR experiments. It has been established by them that the interaction of the ferroelectric sample with the rf field is electrostatic in nature [33]. However, the relaxation effects produced by this so called piezoelectric coupling was not studied. A study in this direction would involve forming rate equation with the additional terms dealing with the piezoelectric coupling. This work is in progress and would be published elsewhere.

5. Conclusions

Effect of domain-walls on the nuclear spin-lattice relaxation of I = 3/2 quadrupolar nuclei in order-disorder ferroelectrics was studied by representing a 180^0 domain by a one dimensional chain of equidistant I = 3/2 spins having nearest neighbour dipolar coupling. The domain-wall is the region joining two adjacent 180^0 domains, and the polarization undergoes a reversal while traversing the domain-wall. It means that if we visualize the sample to be made of thin slices parallel to the domain, then the polarization in the slices would be almost parallel to each other in the domain, whereas, the polarization in the slices in the region of the domain wall would possess larger relative tilts as one moves from one domain to the other. As a result the thermally activated local motions at and near the domain-walls would be easier as compared to those deep inside the domain. Therefore, at a certain temperature, the nuclei near the domain-walls would have larger relaxation probability due to fluctuating electric field gradients, as compared to those situated in the interior of the domain. This would lead to spin-diffusion from domain-walls. Rate equations were formed for spin-populations of $I = 3/2$ spin systems having quadrupolar splitting. These coupled equations were solved for the condition that the external magnetic field is perpendicular to the axis along which the chain of nuclei is directed and cross-relaxation is absent. After a pulse excitation, the population differences between the adjacent levels were found to vary with time in a non-exponential way and for times, much longer as compared to the domain diffusion time, the variation followed a power law dependence. It was found that the present theory explains qualitatively well the low temperature relaxation data of ^{23}Na in single crystal of ferroelectric $NaNO_2$ and successfully predicts the influence of domain-walls on the over-all relaxation especially at low temperatures. Our results can be applied to other- order disorder ferroelectrics having $I = 3/2$ spin-system.

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Appendix

The one-dimensional Laplace transform of a function $f(t)$ is defined as [21, 22]

$$F(s)=\mathcal{L}\{f(t)\}=\int_0^\infty e^{-st}f(t)\,\mathrm{d}t,$$

whereas $\mathcal{L}$ is a Laplace variable.

The error function is a special function and defined as (22)

$$erf\,z=(2/\sqrt{\pi})\int_0^z \exp(-t^2)f(t)\,\mathrm{d}t.$$

The complementary error function erfc is given by

$$erfc\,z=(2/\sqrt{\pi})\int_z^\infty \exp(-t^2)f(t)\,\mathrm{d}t.$$

The numerical expansion of complex error function is given by

$$erf\,(x+iy)=erf\,x+\frac{\exp(-x^2)}{2\pi x}[(1-\cos 2xy)+i\sin 2xy]$$

$$+(2/\sqrt{\pi})\exp(-x^2)\sum_{n=1}^{\infty}\frac{\exp(-n^2/4)}{n^2+4x^2}$$

$$[f_n(x,y)+ig_n(x,y)]+\in(x,y),$$

where

$$f_n(x,y)=2x-2x\cosh ny.\cos 2xy+n\sinh ny.\sin 2xy,$$

$$g_n(x,y)=2x\cosh ny.\sin 2xy+n\sinh ny.\cos 2xy,$$

$$|\in(x,y)|=10^{-16}\,|erf\,(x+iy)|.$$